

METHANOL SYNTHESIS FROM SYNGAS IN A SLURRY REACTOR

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Introduction

The synthesis of methanol from CO and H₂ has become more important since methanol is one of the materials that can substitute the forthcoming depletion of petroleum. Industrially, methanol is produced catalytically on copper-containing catalysts such as Cu/ZnO/Al₂O₃ and Cu/ZnO/Cr₂O₃ from synthesis gas containing carbon monoxide, carbon dioxide and hydrogen in a gas-phase process at high pressures and temperatures. The synthesis gas is usually produced by the steam reforming of natural gas or other hydrocarbons or coals.

In the gas phase process, syngas reacts on the surface of the catalysts in a fixed bed reactor. In this type of reactor, the control of the reaction temperature uses the recycling of excess synthesis gas for the removal of reaction heat. H₂-rich synthesis gas is the preferred media for heat removal because the heat capacity of H₂ is much larger than that of CO. Therefore, the one-pass CO conversion is kept at a relatively low level. The recycling and compression of synthesis gas result in a huge energy consumption^[1].

To overcome these disadvantages of the gas phase process, liquid phase processes for methanol production have been developed.^[2] A higher one-pass CO conversion is obtained in the liquid phase processes, and these new processes also confer technical advantages when CO-rich synthesis gas is used as the feedstock.

In this work, we report the development of a new catalyst (denoted LP201) which gives a high CO conversion without any decrease in activity in 1000 hour operation in a slurry reactor for the synthesis of methanol. The syntheses of methanol in a slurry reactor and a fixed bed reactor are compared and the deactivation of the catalyst in the gas-phase process is discussed.

Experimental

Catalyst preparation. The catalyst, denoted as LP201, has a molar ratio of copper, zinc, aluminum and zirconium of 5:4:0.8:0.2 and was prepared by a co-precipitation method described elsewhere.

Catalyst characterization. The BET specific area of the catalyst samples were measured in a Micrometrics ASAP 2400 apparatus by nitrogen adsorption. The specific area of the catalyst LP201 is 93 m²/g. Thermogravimetric analysis was performed on a WCT-2A thermogravimetric apparatus and infrared spectroscopy on a Nicolet FT-IR spectrometer.

Catalyst activity. CO (containing 4.2% CO₂) and H₂ were mixed and fed into a 1000 ml stirred autoclave with a series of controllers which provide precise control and measurement of temperature (± 1 K), agitator speed and pressure (Autoclave Engineers, USA). After reaction, the mixture is processed by a high-pressure gas-liquid separator. The gas phase flows out through a back-pressure regulator and is analyzed on-line by gas chromatography. The flow rate is measured with a wet flow meter. The liquid phase flows through a needle valve and enters a normal-pressure gas-liquid separator. The liquid product (methanol) is weighed and its composition is analyzed by gas chromatography. The solvent is liquid paraffin, whose distillation cut-off temperature is

higher than 573 K. The catalysts are LP201 or C302 (manufactured in China) used with particle sizes of 150-180 mesh. Before use for methanol synthesis, they were reduced in H₂/N₂ (3.4% H₂) at 240°C and 0.8 MPa.

Results and Discussion

The activities of the LP201 and commercial C302 catalysts in a mechanical agitated slurry reactor are compared. The result is shown in Figure 1. It can be seen that the activity of the LP201 catalyst is much higher than that of the commercial C302 catalyst. When LP201 is used, its syngas conversion at the lower pressure of 4 MPa is higher than that of C302 at 6 MPa. This indicates that the LP201 catalyst is suitable for the large scale synthesis of methanol in a slurry reactor.

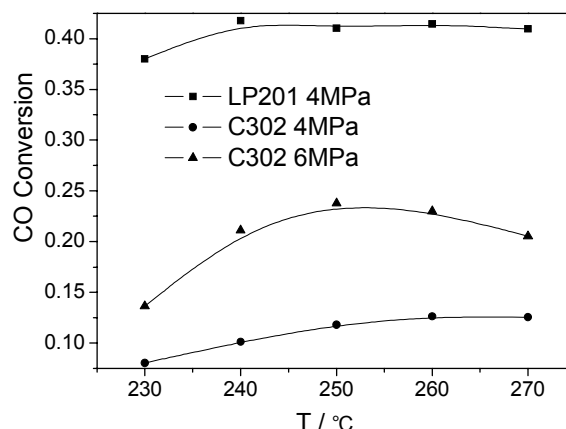


Figure 1. Comparison of the activities of LP201 and C302 at a space velocity of 3000 ml.gcat⁻¹.hr⁻¹ and H₂/ (CO+CO₂) of 2

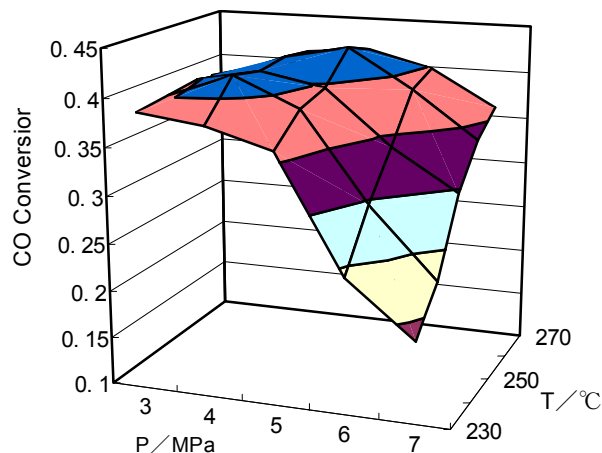


Figure 2. Influence of temperature and pressure on CO conversion at a space velocity of 3000 ml.gcat⁻¹.hr⁻¹ and H₂/ (CO+CO₂) of 2

Figure 2 shows the influence of temperature and pressure on CO conversion in a slurry reactor. There exist different phenomena at high and low pressure conditions. When the pressure is relatively low, with an increase in temperature, the change in CO conversion is not monotonic, and the trend is that of an increase followed by a decrease, with the maximum conversion appearing near 250 °C. This

phenomenon is in agreement with many works in the literature^[3, 4] and our previous works.^[5] As the reaction temperature increases, the reaction rate gets higher and leads to the increase of CO conversion. However, methanol synthesis is an exothermic reaction, and a low temperature is more beneficial for methanol synthesis. With continual increase in the reaction temperature, the conversion does not continue to increase because of thermodynamic limitation, but a decreasing trend will even appear. When the system pressure is relative high, because of the relatively low CO conversion, the system is far from thermodynamic equilibrium and under the control of reaction kinetics. In this case, CO conversion increases monotonically with an increase in temperature.

In the whole temperature range studied, with an increase in pressure, CO conversion first increases and then decreases. Methanol synthesis is a volume-decreasing reaction, and a high pressure benefits methanol generation, but when the pressure increases beyond a certain pressure, methanol accumulates in the liquid phase, which leads to a check on methanol synthesis and the CO conversion decreases.

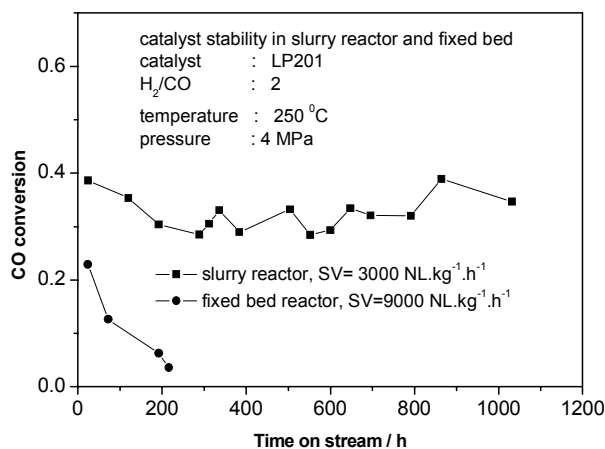


Figure 3. Stability of LP201 catalyst in a slurry reactor and a fixed bed reactor.

LP201 has a higher catalytic activity and good stability in a slurry reactor, as shown in Figure 3. The one-pass CO conversion is still higher than 30% after a 1000-hour lifetime experiment. However, in a fixed bed reactor, the catalyst activity shows an obvious decreasing trend at a space velocity of 9000 L.kg⁻¹.h⁻¹. This phenomenon shows the advantage of a slurry reactor compared with a fixed bed, and the liquid phase methanol synthesis is more suitable for the large-scale industrial application.

To understand the deactivation of catalyst LP201 in the fixed bed, thermogravimetric analysis (TGA) and infrared spectroscopy studies were carried out. Figure 4 shows the results of TGA. The TG curve shows three regions of weight loss: 20~110, 110~300 and 600~800°C, which are attributed to water loss and carbon combustion of the deactivated catalyst, respectively. Meanwhile, an endothermal peak around 80°C, and two exothermal peaks around 300 and 700°C appear in differential thermal analysis (DTA) that are related to the thermo-gravity losses. These indicate the existence of carbon on the deactivated sample and the two exothermal peaks around 300 and 700°C in DTA represent different types of carbon^[6]. Figure 5 shows the FT-IR spectra of LP201 catalyst before reduction (A), after reduction (B), after deactivation (C) and the sample after TGA of the deactivated catalyst (D). The surface structure of the deactivated catalyst is very different from the LP201 catalyst after reduction and

before methanol synthesis and the change in the structure of the deactivated catalyst is irreversible. This suggests that an irreversible change in the structure of catalyst and carbon deposition during the gas-phase methanol synthesis led to the deactivation of the catalyst.

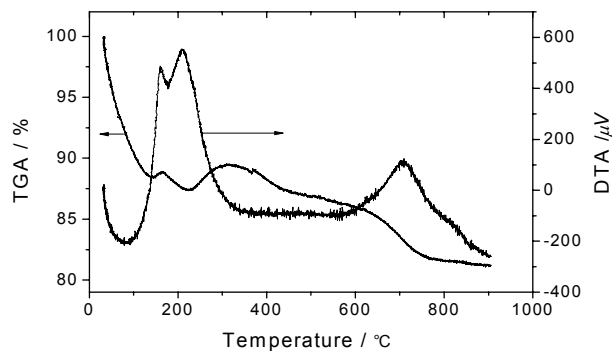


Figure 4. TGA and DTA of deactivated LP201 catalyst

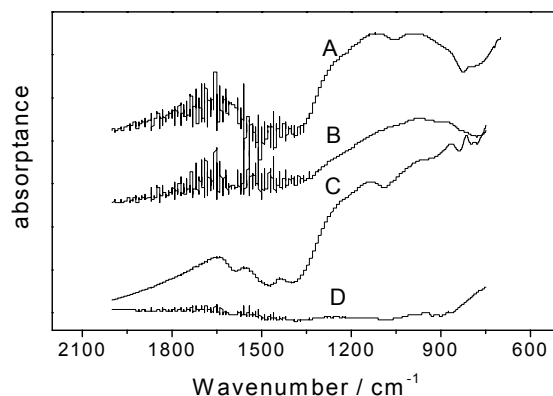


Figure 5. Infrared spectra of LP201 catalyst
A-before reduction, B-after reduction, C-after deactivation, D-the sample after TGA of the deactivated catalyst

References

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